

# Supporting Information: Comprehensive Simultaneous Shipboard and Airborne Characterization of Exhaust from a Modern Container Ship at Sea

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Supporting Information includes 6 pages with 3 figures

## **S1. Shipboard Platform Test Methods**

**S1.1 Measurement of Stack Gases.** The concentrations of gases in the raw exhaust and the dilution tunnel were measured with a Horiba PG-250 portable multi-gas analyzer. For quality control, analyzer checks with calibration gases both before and after each test were made to check for drift. The SO<sub>2</sub> data presented here are calculated from the sulfur level in the fuel as suggested by the certification method in ISO 8178 (15).

**S1.2 Measurement of Particulate Matter (PM) mass and Ions.** The mass concentrations of PM<sub>2.5</sub> and ions were acquired by analysis of particulate matter collected on 47 mm diameter 2 µm pore Teflo filters (Pall Gelman, Ann Arbor, MI). The filters were measured for net gains using a Cahn C-35 (Madison, WI) microbalance following the weighing procedure guidelines of the Code of Federal Regulations (CFR) (16). Before and after collection, the filters were conditioned for 24 h in an environmentally-controlled room (RH = 40%, T = 25 °C) and weighed daily until two consecutive weight measurements were within 3 µg. Finally, the filters were extracted with HPLC grade water and isopropyl alcohol and analyzed for sulfate ions using a Dionex DX-120 ion chromatograph. Real time measurements of total particle mass were made by a Dekati Mass Monitor (DMM-230) with 1 s time resolution (20).

**S1.3 Measurement of Particle-Phase Elemental and Organic Carbon.** OC/EC analysis was performed on samples collected on 2500 QAT-UP Tissuquartz Pall (Ann Arbor, MI) 47 mm filters that were preconditioned at 600 °C for 5 h. A 1.5 cm<sup>2</sup> punch

was cut out from the quartz filter and analyzed with a Sunset Laboratory (Forest Grove, OR) Thermal/Optical Carbon Aerosol Analyzer according to the NIOSH 5040 reference method (19).

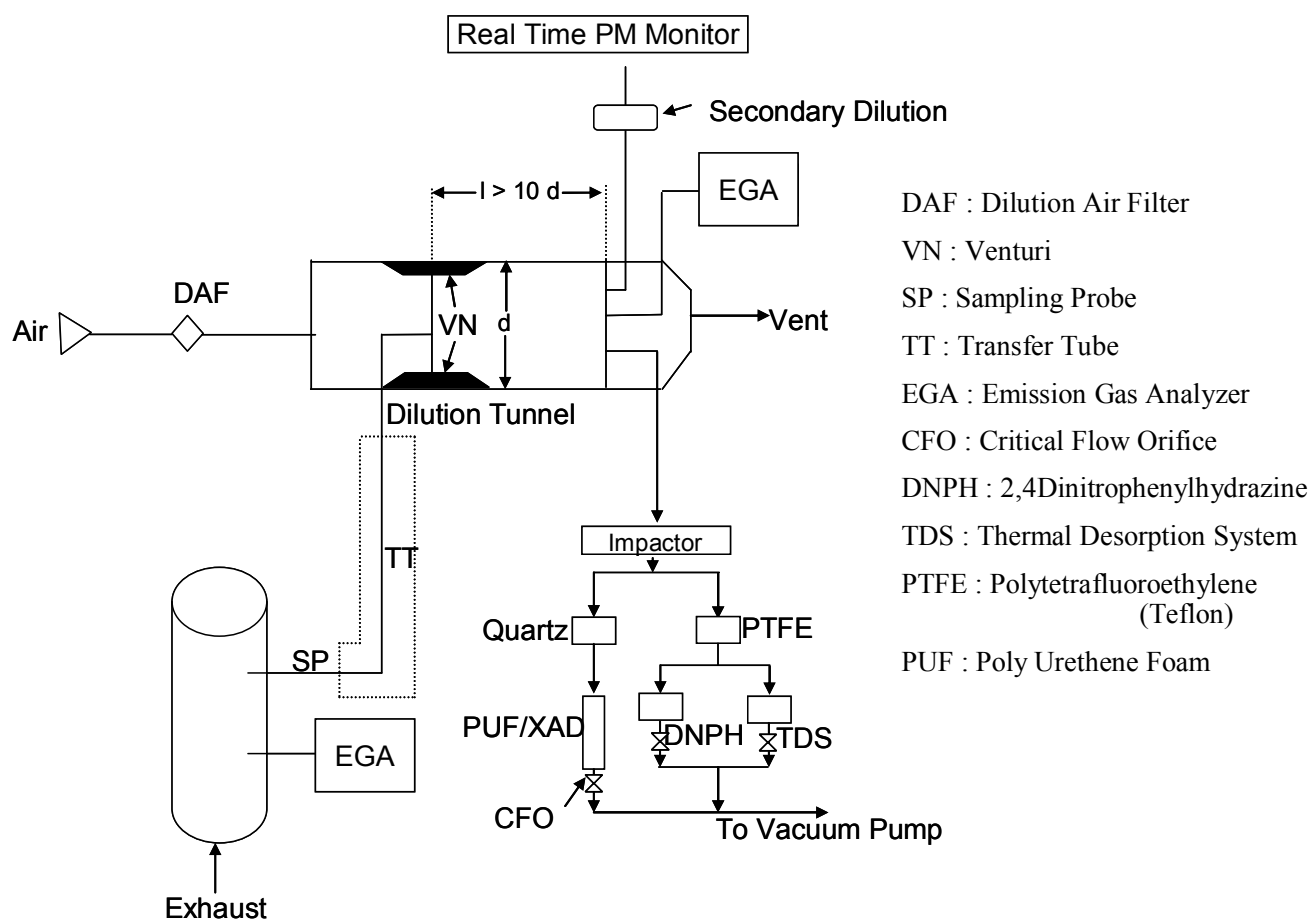
**S1.4 Measurement of Size-Resolved Particulate Composition.** A ten stage rotating Micro-Orifice Uniform Deposit Impactor (MOUDI) (MDI-110-R-366, MN) was used in order to obtain size resolved PM. The Model 110 provides cut-point diameters of 18, 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18, 0.1, and 0.056  $\mu\text{m}$ . Aluminium (Al) filter substrates were used on all the upper stages and quartz filter substrate was used as after filter. The Al filters were measured for net PM gains using a Cahn C-35 (Madison, WI) microbalance. The quartz after filter ( $<56\text{nm}$ ) cannot be accurately weighed because of loss of quartz fibers during the sampling to the o-ring seal. The filters were subsequently analyzed for EC, OC, and sulfate following the standard procedures described in the previous section. This enabled the determination of the chemical composition of PM among various particle size bins.

**S1.5 Measurement of Carbonyls.** Carbonyls were collected on 2,4-dinitrophenylhydrazine (DNPH) coated silica cartridges (Waters Corp., Milford, MA) behind the Teflon filter as shown in Figure 1. A critical flow orifice was used to control the 1.0 liter per minute flow through the cartridge. Sampled cartridges were extracted using 5 mL of acetonitrile and injected into an Agilent 1100 series high performance liquid chromatograph (HPLC) equipped with a diode array detector. The column used

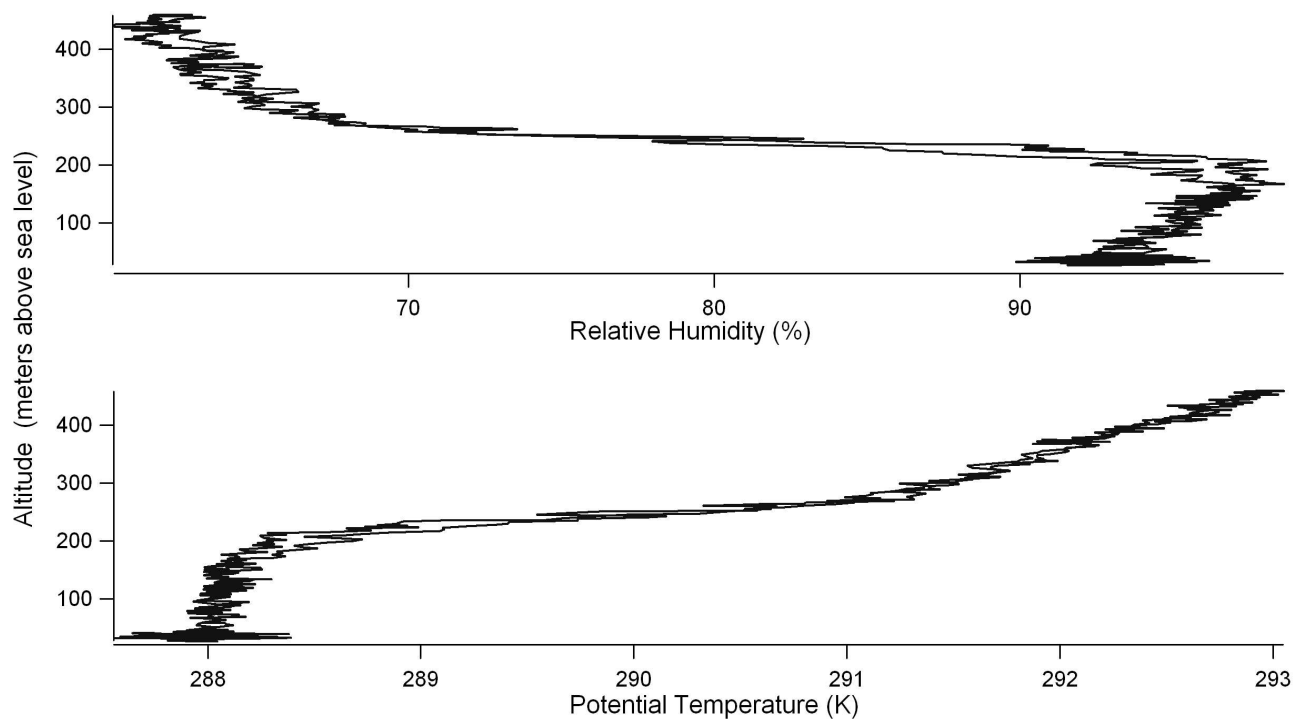
was a 5  $\mu\text{m}$  Deltabond AK resolution (200 cm x 4.6 mm ID) with upstream guard column. The HPLC sample injection and operating conditions followed the specifications in the SAE 930142HP protocol (18).

**S1.6 C<sub>10</sub> to C<sub>30</sub> Hydrocarbons, Including Naphthalene and PAHs.** The diluted exhaust was collected through a quartz filter and into a column packed with polyurethane foam (PUF)/XAD-4 resin. A portion of the quartz filter was used to analyze for elemental and organic carbon, as described in the previous section. Both the PUF/XAD-4 cartridge and the remainder of the quartz filter were extracted with methylene chloride and analyzed using a modified method EPA TO13A protocol (GC-MS analysis) to determine total emission rates for PAHs and n-alkanes. Details on the analysis method are found in Shah et al. (17).

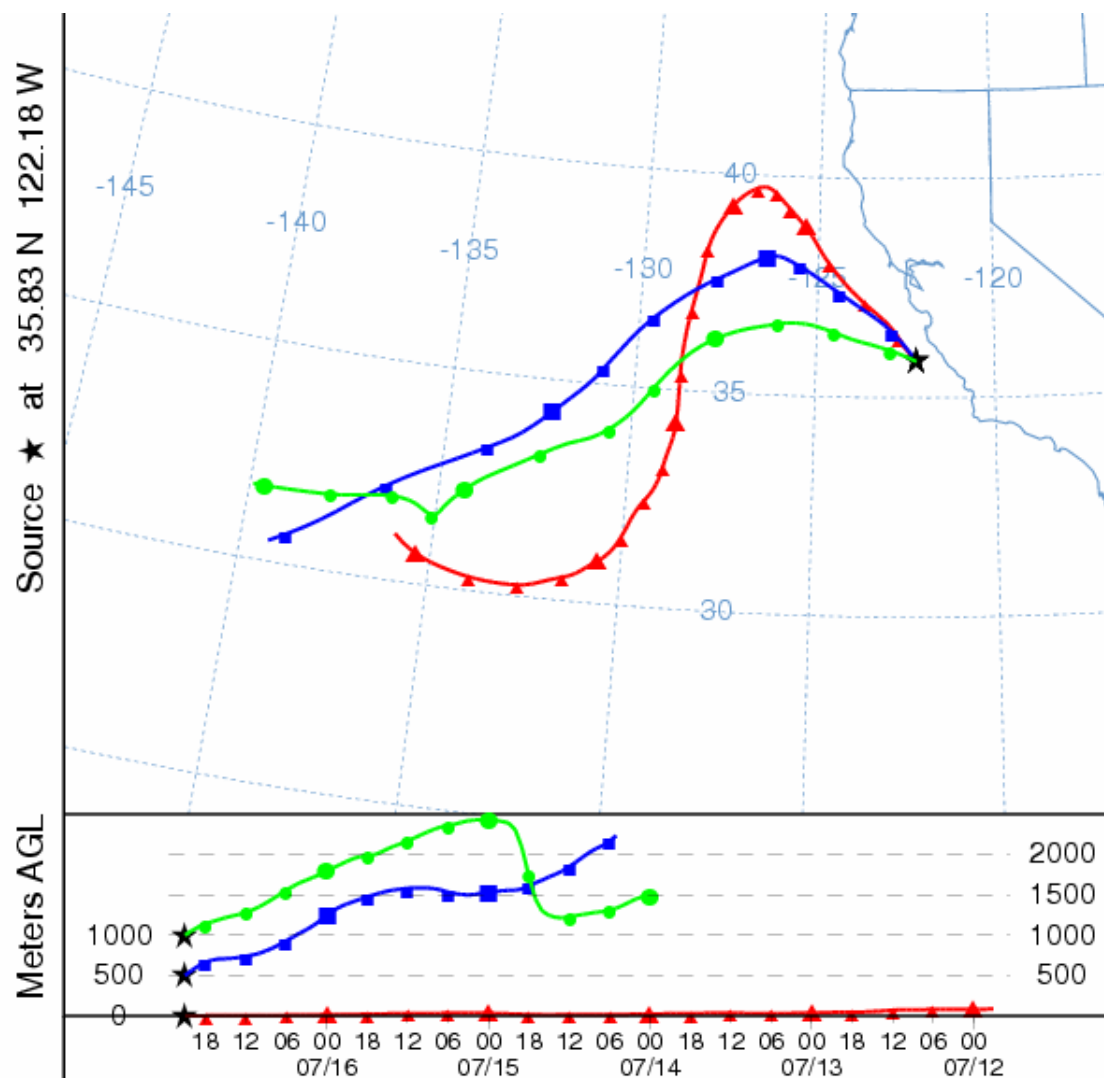
**S1.7 1,3 Butadiene; Benzene; Toluene; Ethylbenzene and Xylenes.** Gaseous organics from C<sub>4</sub> (butadiene) through C<sub>12</sub> were collected and concentrated on a multi-bed adsorbent column, including molecular sieve, activated charcoal, and carbotrap resin. The most volatile compounds adsorb first; the remaining compounds adsorb sequentially in relation to their volatility. The GC sample injection, column, and operating condition were set up according to the specifications of SAE 930142HP Method-2 for C<sub>4</sub>-C<sub>12</sub> hydrocarbons.



**Figure S1:** Flow Diagram of the Sampling System used on-board the container ship. No transfer tube was used in this study.



**Figure S2:** Vertical profiles of relative humidity and potential temperature during the study. Each plot has two traces, representing data from an ascent and a descent through the marine boundary layer.



**Figure S3:** NOAA Hysplit three-day back trajectory for the air mass present during the study. At all altitudes, the air originates from the west and does not appear to be subject to recent continental influence.